National Defence / Défense nationale

UNCLASSIFIED

UNLIMITED

DREV REPORT 4740/94
MARCH 1994

CRDV RAPPORT 4740/94
MARS 1994

[redacted]

PRECISE EQUIVALENT WEIGHT DETERMINATION OF BRANCHED GLYCIDYL AZIDE POLYMERS BY NMR SPECTROSCOPY

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SANS CLASSIFICATION

UNLIMITED

104-07256/

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Québec, Canada March/mars 1994

SANS CLASSIFICATION

ABSTRACT

In order to develop an exact equivalent weight method for branched glycidyl azide polymer (GAP), an acetylation study of linear polyepichlorohydrin (PECH), linear and branched GAPs was made by using different alcohol substituents such as TFA or HFA. It was found by IR spectroscopy of the derivatives that TFA and HFA were not strong enough for a complete reaction on branched GAPs. This incomplete reaction was responsible for the unsuccessful equivalent weight determination of those derivatives.

A better reaction condition was obtained with acetic anhydride/pyridine heated overnight at 95°C, followed by coevaporations with toluene. Acetylation was complete for PECH while for GAPs it seems, by the IR band at 3360 cm^{-1}, that it was not even with this strong acetylation. Deuterium exchange experiments with D_2O proved that this IR absorption was an overtone or a combination band and that acetylation was in fact completed.

Complete acetylation reactions were tried on fourteen prepolymers with different structures including the branched GAPs. The OH equivalent weights of these prepolymers were then determined by ^1H NMR spectroscopy of the acetyl derivatives. The precision of the method was between 5-10% and the sensitivity limited a precise determination to equivalent weight below 5 000. The values determined and this method are now currently used for propergol and explosive formulations by chemists and engineers at DREV.

RÉSUMÉ

Dans le but de développer une méthode précise de détermination des poids équivalents du polyazoture de glycidyle (PAG) ramifié, une étude d'acétylation du polyépichlorohydrine (PECH) linéaire, des PAG linéaires et ramifiés a été effectuée en utilisant les dérivés TFA et HFA. On a constaté par la spectroscopie IR que ces dérivés ne sont pas suffisamment réactifs pour provoquer une réaction complète avec le PAG ramifié. Cette réaction incomplète avec les dérivés était responsable des mauvais équivalents OH déterminés à l'aide de cette méthode.

De meilleures conditions ont été obtenues en utilisant de l'anhydride acétique/pyridine chauffé une nuit à 95°C, puis en provoquant des coévaporations au toluène. Cette acétylation était complète avec le PECH, tandis que pour les

PAG une bande IR à 3360 cm^{-1} semblait affirmer que la réaction d'acétylation n'était pas complète. Des expériences d'échange avec le D_2O basique ont montré que l'absorption pouvait être attribuable à une harmonique ou à une combinaison et que l'acétylation était effectivement complète.

Des acétylations complètes ont alors été effectuées sur quatorze prépolymères de structures variées, incluant le PAG ramifié. Les masses équivalentes de ces prépolymères ont ensuite été déterminées par RMN ^1H. La précision de la méthode se situait entre 5 et 10%, tandis que la sensibilité limitait la détermination précise à des masses équivalentes inférieures à 5 000. Les valeurs déterminées et la méthode sont maintenant couramments utilisées par les chimistes et les ingénieurs du CRDV pour les compositions de propergols et d'explosifs.

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TABLE I

EXECUTIVE SUMMARY

Over the last 25 years dramatic accidents with stored ammunition have happened during fires, handling and transportation. In most cases, some unplanned stimuli such as thermal, mechanical, electrical and shock wave were responsible for the catastrophic events. It is now clear to the Canadian Forces as well as to Canadian industries that the present goals should be more oriented toward munitions of low vulnerability. There is also increasing attention toward low-smoke signatures and low-polluting propellants.

In the light of these considerations, DREV has initiated a research and development program for developing low-sensitivity ammunitions by using energetic solid crystal with lower energy and less sensitivity. In order to compensate for the loss of energy from the solid crystal, the conventional inert binder is replaced by an energetic binder such as glycidyl azide polymer. The final goal is to keep the same energy but with a reduced sensitivity.

Glycidyl azide polymer has the advantage of being compatible with RDX for explosive development and with ammonium nitrate for rocket propellants. It is expected that explosives or gun propellants with RDX will lead to lower sensitivity materials while, for rocket propellants, the use of ammonium nitrate will respond to the need for low-sensitivity, low-signature and low-polluting propellants.

During the formulation of plastic-bonded explosives or propellants, the alcohol of the glycidyl azide polymer reacts with isocyanate compounds and leads to a rubbery binder that gives mechanical integrity. However, before mixing, the added quantity of isocyanate is strongly governed by the quantity of alcohol reactive groups present in the glycidyl azide polymer.

Consequently, knowing the exact alcohol equivalent weight of the glycidyl azide polymer is of fundamental importance for the development of low-vulnerability plastic bonded explosives as well as for low-sensitivity solid propellants. For the determination, many equivalent weight methods were available, such as IR spectroscopy, titration and NMR spectroscopy, but none of these showed satisfactory results for the branched glycidyl azide polymer.

This report present the complete development of an exact equivalent weight determination for branched glycidyl azide polymers. The values determined with this method are now currently used for propergol and explosive formulations by chemists and engineers at DREV.

LIST OF SYMBOLS

DMF	:	N,N-dimethylformamide
DMSO	:	dimethylsulfoxide
Ew	:	Equivalent weight
FID	:	Free Induction Decay of the NMR signal
GAP	:	Glycidyl Azide Polymer
HFA	:	hexafluoroacetone
HTPB	:	hydroxyl-terminated polybutadiene
IR	:	infrared spectroscopy
Mw	:	molecular weight
NMR	:	Nuclear Magnetic Resonances
^{13}C NMR	:	Nuclear Magnetic Resonance spectroscopy of the carbon atoms
^{1}H NMR	:	Nuclear Magnetic Resonance spectroscopy of the Hydrogen atoms
PAG	:	polyazoture de glycidyle
PECH	:	polyépichlorohydrine
RMN	:	résonance magnétique nucléaire
TFA	:	trifluoroacetic anhydride
THF	:	tetrahydrofurane
ν_{O-D}	:	IR stretching deuterated alcohol band

1.0 INTRODUCTION

Glycidyl azide polymer (GAP) containing azido groups (N_3) and secondary hydroxyl functions (-CH-OH) is an energetic prepolymer that can be cured with isocyanates and solid oxidizers for rocket propellant technology. This class of prepolymer with a linear structure was prepared from polyepichlorohydrin (PECH) for the first time and patented in Japan by T. Nishikubo et al. (Ref. 1), subsequently named GAP and patented in the USA by Frankel et al. (Refs. 2 to 5). A faster process (Refs. 6 and 7) using a single step is also known for the synthesis of linear GAPs. A GAP with a branched structure containing mainly secondary alcohols has been developed at DREV and patented by Ahad in several countries (Refs. 8 and 9). More recently, some GAP prepolymers containing a primary alcohol function (CH_2OH) and a linear structure were synthetised and characterised by Ampleman and Désilets (Refs. 10 to 12) to increase the curing speed during the formulation (Refs. 13 and 14).

During the processing of propellants or explosives based on GAP, the principal reaction step involved is that between the alcohol groups (OH) of the GAP prepolymer and the isocyanates (NCO), which lead to an elastomeric polyurethane binder. Research in this area has largely proved that the mechanical integrity and properties of the final formulation is strongly dependent on the NCO/OH ratio. Consequently, an important parameter to be characterised is the quantity of alcohol function present in the prepolymer described by the OH equivalent weight (Ew).

Currently, three methods are available for the determination of Ew : titration (Ref. 15), NMR spectroscopy (Ref. 16) and IR spectroscopy (Ref. 17). The titration method uses an acetylation reaction of the prepolymer followed by acid/base titration of the acetic acid formed. However, the volatility of acetic acid may cause errors during the determination and some care must be taken by using tight corked container during the acetylation reaction. Another imprecision with this method is that the aqueous acid/base titration may cause some insolubility of the organic prepolymer and, as a result, the change and formation of a stable colour during the titration is not as sharp as expected. As with the titration method, the NMR method requires the synthesis of a derivative of the prepolymer which is then analysed by NMR spectroscopy. Many derivative groups, like hexafluoroacetone (HFA) (Ref. 18), trifluoroacetic anhydride (TFA), (Ref 19) were used and the NMR quantification is made by the integration of the shifted proton signal of the derivative. By comparison, the IR method has an important advantage over titration and NMR determinations because no reactions are needed. But, due to the presence of an additional hump in the FTIR spectrum of THF solution GAP samples (Ref. 20) the IR method could not be used directly for these types of prepolymers. Consequently, the IR method needs "standard GAP" samples for which the Ew has been previously determined in order to construct a calibration curve.

Both titration and NMR methods involve an acetylation reaction of the prepolymer while the IR method need a calibration curve. It appears that the two first methods are the most exact ones, but if the acetylation reaction is not completed the Ew determination is wrong. Consequently,

an important factor to be verified is to know if the reaction is completed and if not, better reaction conditions must be found. Because of this, an acetylation study of linear polyepichlorohydrin (PECH), linear and branched GAPs has been made in order to develop a good equivalent weight method for branched GAPs. The study reported herein covers two aspects of the equivalent weight method. The first one is the acetylation reaction, which will be studied by IR and NMR spectroscopies, and the second is the equivalent weight determination of some typical samples by NMR. The aim of this systematic study was to develop a precise equivalent weight method for formulation of propergols or explosives based on branched GAPs. This study was performed at DREV between August 1989 and December 1991 under Project 32C, Rockets and Missiles.

2.0 EXPERIMENTAL

2.1 Experimental Acetylation Studies

The acetylation of PECH was done as follows: 4 g (0.003 mol of alcohol) of linear PECH HX-102 (Ew=1200 g/mol of alcohol function) purchased from the 3M Co., were dissolved in 20 mL of pyridine and 2.5 mL (0.027 mol) of acetic anhydride were added. The mixture was corked and heated at 95°C for 12 hours. The resulting solution was cooled at room temperature and evaporated under vacuum (1 to 5 torr). The acetic acid-pyridine complex was removed by dissolution of the prepolymer in 50 mL of toluene followed by a coevaporation under vacuum. This last coevaporation operation was repeated twice and completed with an evaporation under higher vacuum (0.1 to 1 torr) using a mechanical pump. No traces of pyridine, acetic anhydride

(Ac_2O) or acetic acid (AcOH) were detected by IR (C=O of Ac_2O at 1810 cm^{-1}, C=O of AcOH at 1710 cm^{-1}) and by NMR spectroscopies(in ^{13}C spectra no C=O acid 210-180 ppm, in ^{1}H spectra no acidic protons in the region between 8 and 14 ppm). The prepolymer was dissolved in 55 mL of dichloromethane, dried with anhydrous magnesium sulfate, filtered and kept dry with 4 Å molecular sieves in dichloromethane. The IR spectra were then acquired in dichloromethane under an anhydrous nitrogen atmosphere.

Acetylations were reproduced on linear and branched GAPs, and the series of GAPs with increased functionality (Refs. 12 to 14). The acetyl derivative of prepolymers with equivalent weights (Ew) between 600 and 2500 g/mol were synthesized using the same procedure and weight of reactive as described for linear PECH. The reaction was also tried for one week with the same quantities of GAPs at 98°C, but it appears that 12 hours were sufficient to obtain a complete reaction. It was found that for long-term reactional conditions (one week), the prepolymer may decompose or recombine.

HFA derivative was made based on the procedure described in a previous report by Druet and Boucher (Ref. 21). TFA derivatives were synthetised according to the following procedure (Ref. 21) : 0.035 g of branched GAP was dissolved in 1 mL of $CDCl_3$ and reacted with 0.8 mL of TFA for 3 hours at 35°C. To obtain better conditions for branched GAPs, many other trials were made by reducing the quantity of TFA during the derivative synthesis (between 0.03 and 0.1 mL of TFA).

To acquire the IR spectrum of the branched GAP-TFA derivative, three extractions (water:dichloromethane) were made. The dichloromethane phase was dried with $MgSO_4$ followed by 4 Å molecular sieves and the derivative was isolated by evaporation of the solvent under vacuum (0.1 to 1 torr).

The tosyl derivative of branched GAPs was made according to the following procedure : 1 g of GAP was dissolved in pyridine and 1 g of p-toluenesulfonylchloride was added. The solution was kept overnight at room temperature and the mixture was transferred into dichloromethane. Three extractions were made with water at room temperature. Finally, the organic phase was dried with $MgSO_4$ followed by evaporation under vacuum (0.1 to 1 torr).

The tert-butyldimethylsilyl derivative was synthetised by reacting 2 g of linear PECH HX-102 in a solution containing 1.8 g of t-butyldimethylsilyl chloride dissolved in 2 mL of DMF. After adding 1.6 g of imidazole, the reacting mixture was heated at 40°C for a period of 24 hours. The mixture was cooled at room temperature and diluted with 20 mL of dichloromethane. The organic solution was extracted with 10 mL of water followed by successive extractions with 10 mL of HCl 1N and with a 10 mL of $NaHCO_3$ solution. The final organic phase was dried with $MgSO_4$ and evaporated under vacuum (0.1 to 1 torr).

The D_2O exchange study of both linear and branched GAPs was made by dissolving 1 g of acetylated GAP in 10 ml of dichloromethane. The solution was washed with 10 mL of D_2O and the dichloromethane layer was separated and dried with $MgSO_4$, filtered and dried on 4 Å molecular sieves. The IR

spectroscopy was then carried out on this solution under anhydrous nitrogen conditions. Two other deuterium exchange studies were also made using the same procedure with the exception that the washing step was made with a basic solution of K_2CO_3 or NaOH in D_2O.

Azidation of the acetylated linear PECH was made by dissolving 2.8 g of the acetylated PECH in 10 ml of DMSO. The solution heated at 70°C was reacted with 2.0 g (1 eq.) of sodium azide and kept overnight under these conditions. The solution was then cooled at room temperature, diluted with 100 mL of dichloromethane and extracted three times with 200 mL of an aqueous NaCl 10% solution. The organic phase was dried with $MgSO_4$, filtered and kept dry with 4 Å molecular sieves. After 3 hours on 4 Å sieves , the IR Spectroscopy was then carried out under total anhydrous nitrogen conditions.

2.2 Experimental IR and NMR Spectroscopies :

IR spectra were acquired in dichloromethane under nitrogen atmosphere using a sodium chloride cell of 0.5 mm thickness with a Biorad Fourier Transform Spectrometer FTS-40 equipped with a DTGS detector. A reference background correction spectrum was made in dichloromethane and used for solvent substraction of each spectrum of the study. Baseline corrections were also applied to all final spectra.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker WP-200MHz NMR spectrometer with 16 K of memory. Quantitative ^{13}C spectra were acquired with inversed gated decoupling pulse sequence (ref. 22) using a delay of 7 s.

For ^{1}H spectra a single pulse or many pulses with a relaxation delay of 2 s were used for reliable integrations. An exponential function was applied to each FID NMR signal for improvement of the signal-to-noise ratio and a baseline correction was then made for precise integration measurements.

Typical NMR chemical shifts in δppm for acetylated PECH and GAPs were as follows:

^{1}H and ^{13}C denote NMR spectral data of proton and carbon of the chemical structure.
Assignation of peaks related to the structure are between parentheses.
Signal types are denoted : m=multiplet, s=singlet,

Acetylated PECH ^{1}H δppm: 5.1(m, CH-OAc), 3.5-3.9(m, CHO, CH_2O, CH_2Cl), 2.1(s, O-Acetate).
^{13}C δppm : 76-78(CHO), 68-71(CH_2O), 43-45(CH_2Cl), 21(O-Acetate).

Acetylated GAPs ^{1}H δppm : 5.1(m, CH-OAc), 3.5-4.0(m, CHO, CH_2O), 3.2-3.4(m, CH_2N_3), 2.1(s, O-Acetate).
^{13}C δppm: 78(CHO), 68-71(CH_2O), 50-52(CH_2N_3), 21(O-Acetate).

2.3 The Equivalent Weight Method by NMR

The reaction procedure chosen for the equivalent weight determination was based on results from the acetylation study described in Section 2.1. Acetylation of prepolymers for the determination of the equivalent weights involved

reacting 0.23 g of prepolymer with 0.4 mL of acetic anhydride in 5 mL of pyridine at 95°C in a corked container for 12 hours. Evaporation of pyridine was done by a first evaporation under vacuum (1 to 5 torr). Residual pyridine, acetic anhydride and acetic acid were removed by dissolution of the acetyl prepolymer in 30 mL of toluene and coevaporating under vacuum (1 to 5 torr). This last coevaporation step was repeated twice and completed with a final evaporation under higher vacuum (0.1 to 1 torr) using a mechanical pump.

Acetylated derivatives were dissolved in $CDCl_3$ and the ^1H NMR spectra were acquired. The equivalent weight determination was made by integrating the large intensity of the prepolymer peaks in the region 3.5-4.0 ppm followed by the integration of the acetyl group at 2.1 ppm. In most cases, some care must be taken not to integrate the large peak of low intensity located in the region 1.7-2.1 ppm (traces of water in $CDCl_3$). This problem may be overcome by adding a drop of D_2O to chemically exchange and get rid of the undesired peak. The Ew was calculated by the formula described in Section 3.2, "Results and discussion".

3.0 RESULTS AND DISCUSSION

3.1 Acetylation Studies

During this study, the first acetylation reaction carried out was with branched GAP using the conventional TFA derivative. The procedure already developed (Ref. 21) for hydroxyl terminated polybutadiene (HTPB) as well as for linear PECH or linear GAP had shown reliable results. However, for branched GAP the results were totally wrong and

showed a large difference in the equivalent weight values when compared with the results determined by the IR (Ref. 20) or titration (Ref. 15) methods. Many branched GAPs with Ew between 270 and 1200 were tried by using the conventional NMR method with TFA (Ref. 21) and compared with the values determined by the IR method.

A typical example is a value of Ew : 600 by acetylation with TFA compared with Ew: 270 by the IR method. In all cases it was observed that the values determined by acetylation were higher by factors of two to three.

At this stage of the study two hypotheses were postulated. The first one was that branched GAPs could be less soluble in the large excess of TFA and consequently less reactive. The second one was that some alcohol in the branched GAPs could be unreactive with TFA. By a meticulous observation, it appeared that some insoluble branched GAP stayed unreacted on top of the reactive solution. As a consequence of this observation, a better experimental procedure was developed by reducing the quantities of TFA (8 to 30 times lower). By using this major modification the prepolymer was totally soluble, resulting in a better acetylation reaction. Consequently, it changed the values of the equivalent weight but, as concluded later the acetylation was still not complete enough to give exact and precise equivalent weight results. In order to see if the reaction was completed the IR spectrum of the TFA derivative was acquired. As seen on Fig. 1 the broad OH band between 3200 and 3600 cm^{-1} clearly showed that the source of the problem for branched GAPs was mainly due to unreacted alcohol functions. A rough evaluation from the intensity reduction of the IR band concluded that the reaction with

TFA was completed at only 40 to 65%. With a similar approach, it was also found, for the HFA derivative, that the reaction was not completed on branched GAPs.

In order to get a 100% completed reaction, three different derivatives were tried : p-toluenesulfonyl, t-butyldimethyl silyl and acetyl derivatives. The best derivative and conditions found for branched GAPs were with the prepolymer dissolved in a solution of acetic anhydride/pyridine reacting overnight at 95°C.

Figure 2 shows the IR spectra of linear PECH, linear GAP and branched GAP acetylated by the drastic acetic anhydride/pyridine conditions. For linear PECH, the spectrum in Fig. 2a clearly shows a total disappearance of the alcohol band between 3200 and 3600 cm^{-1}, proving that the linear PECH was completely acetylated. By comparison, for both linear and branched GAPs, Figs. 2b and 2c show the presence of a small band at 3360 cm^{-1}, which could indicate, to first approximation, that the acetylation was not completed. As an hypothesis, one could think that this small band come from traces of water in acetylated GAP prepolymers. This possibility was eliminated by doing an extraction with D_2O. If water were present, D_2O would replace H_2O and consequently the IR spectrum would show the disappearance of O-H band and an apparition of a ν_{O-D} stretching in the region at 2400 cm^{-1}. The results of that experiment did not show any disappearance of the unknown band at 3360cm^{-1}.

Two other experiments, which consisted in reacting the possible unreacted alcohols with D_2O under weak basic conditions with K_2CO_3 or also under drastic NaOH conditions,

were tried. The IR spectrum after these treatments did not show any OH ⇌ D_2O exchange in the OH region between 3200 to 3600 cm^{-1}. This last experiment proved that both linear and branched GAPs were totally acetylated and that the unknown band at 3360 cm^{-1} must be of another type than residual alcohol.

As a final and convincing proof the linear PECH, which was already 100% acetylated (Fig. 2a), was transformed to acetylated linear GAP by azidation using NaN_3 in DMSO. Before measuring the IR spectrum of this resulting prepolymer, it was verified, by ^1H and ^{13}C NMR quantitative determinations, that the acetyl group was not affected during the azidation. The IR spectrum of this 100% acetylated linear GAP is shown in Fig. 3 and still has the 3360 cm^{-1} band with an intensity similar to that of acetylated branched GAP (Fig. 2c). This proves, a second time, that the residual band of this 100% acetylated GAP is not of the alcohol type but could possibly come from an overtone or a combination band. The possibility of overtone could come from the C=O of the acetyl function. The combination could also come from the addition of the intense azide antisymmetric stretching band at 2110 cm^{-1} combined with the symmetric azide stretching located at 1280 cm^{-1}, which result in a band at 3360 cm^{-1} (2110 cm^{-1} + 1280 cm^{-1} ≈ 3390 ~ 3360 cm^{-1}.

It is now conclusive that the acetylation under drastic conditions (by acetic anhydride/pyridine at 95°C) is completed for the linear PECH and linear GAP as well as for the branched GAP.

3.2 Equivalent Weight Determinations by NMR

Based on the study described in the last section, a good reaction procedure was developed for a complete acetylation of PECH, linear GAP and branched GAP. Considering that the acetylation is completed, the derivative can be now used for an exact equivalent weight determination by using the NMR spectroscopy of the derivative.

The typical ^1H NMR spectrum of an acetylated branched GAP is shown in Fig. 4. The spectrum is dominated by the intense GAP protons between 3.2 and 4.8 ppm while a small multiplet at 5.2 ppm is due to the α protons of type CH-OAc. When a primary alcohol was present, the α protons from CH_2-OAc were immerged by the large peak of GAP. Nevertheless, the CH_3 protons of the acetyl group at 2.1 ppm are in an isolated region and are shown in the spectrum as a sharp single peak. Consequently, the CH_3 peak is a better candidate for the quantification of the acetyl group which gives the alcohol equivalent weight using the following formula:

$$Ew\ (g/mol) \quad : \quad \frac{I_{GAP}/5 \ X \ Mw}{I_{CH3}/3}$$

Ew : Equivalent weight (g/mol of alcohol).

I_{GAP} : The area of the PECH or GAP peaks in the ^1H spectrum (between 3.5 and 4.0 ppm).

I_{CH3} : The area of the CH_3 acetyl peak in the ^1H spectrum (at 2.1 ppm) .

Mw : Molecular weight of the monomer repetition unity of PECH (Mw = 92.5 g/mol) or GAP (Mw = 99.1 g/mol).

In this equation each intensity is divided by its corresponding quantity of proton (5 for GAP protons : CH_2N_3, CHO, CH_2)(3 for acetate protons from CH_3). In this way, the first ratio of $I_{GAP}/5$ divided by the second ratio $I_{CH3}/3$ gives the number of GAP pattern -(OCH-(CH_2N_3)-CH_2)- for each acetate. Finally, this ratio multiplied by the molecular weight (Mw) of the GAP pattern determines the alcohol equivalent weight.

This simple equation, which does not need an internal standard, assumes that the prepolymer is principally formed of PECH or GAP with a low content of impurities. This assumption was true for all cases of PECH or GAP analysed in this study. Special care has to be taken to avoid the integration of the low intense peak located in the region between 1.7 and 2.1 ppm (water in $CDCl_3$). The determination using the addition of an internal standard like 4-nitroacetophenon was also tried and gave similar results.

The analysis was made on fourteen different prepolymers with structures described in Fig. 5. The results are gathered in Table I and compared with different results from the IR spectroscopic method using a calibration curve with a slope = .0148 (Ref. 20). For example, the method tried on linear PECH or GAP gives similar results (Ew : 1210 and 1200) as determined previously by the IR method (Ew : 1180 and 1175).

By comparison, for structures 3 to 8 with functionality increased by two, three or four and synthetised from PECH HX-102 (Ew: 1210), the expected equivalent weight Ew would be 1210/2 = 605, 1210/3 = 403 and 1210/4 = 303. In fact, the values determined and presented in Table I (doubled, tripled and quadrupled functionalities) were in agreement with the expected structure and proved for the GAP with increased functionality (structures 3 to 8) that the equivalent weight method was also useful for chemical structure confirmation.

The NMR method was also tried on different branched GAPs (nos. 1 to 6 in Table I) and the equivalent weights were used for propellant formulation and showed reliable results (Ref. 23). This last observation proved that the new equivalent weight determination method by NMR was good for the branched GAP. The Ew values reported in Table I and obtained by IR spectroscopy were determined by E. Ahad according to the method described in Ref. 20. By using a calibration curve with a slope = .0148, the Ew values determined by IR for branched GAPs are similar to the Ew values obtained by NMR.

3.3 Precision of the NMR Method

After many determinations, it was found that the precision of the data was mainly related to the care given during the integration procedure. Firstly, the baseline correction is an important factor to be done with meticulous attention and has to be reproduced many times. Secondly, the integration of the NMR peaks after baseline correction

has to be reproduced five to ten times. Also, integration with and without the baseline correction gives an idea of the precision of the data.

The precision of this method was mainly limited to 5-10% based on the difficulty of integrating the acetyl group with a higher precision. For high Ew values (> 5 000) the acetyl peak was of low intensity and consequently the precise quantification became difficult. However, due to the sharp peak integration, the sensitivity was approximatively increased by a factor of ten compared with the former method using TFA or HFA(Ref. 21).

It must be mentioned that, for both the titration and IR methods, water was a disturbing factor for the alcohol equivalent weight determination, while for the NMR method water is transforming into acetic acid and removed during the coevaporation procedure.

4.0 CONCLUSION

This exhaustive acetylation study has largely proved that TFA and HFA were not appropriate for an equivalent weight determination of branched GAPs. The uncomplete (TFA or HFA) reaction was demonstrated by the residual alcohol band present in the IR spectrum. It was concluded that the incomplete acetylation reaction for branched GAPs using TFA or HFA derivatives was responsible for the wrong equivalent weight determination by NMR. Consequently, for branched GAPs a better derivative and/or reactional condition had to be found in order to determine precisely by NMR the equivalent weight.

The best reaction conditions found for branched GAPs were with acetic anhydride/pyridine reacting overnight at 95°C. Despite drastic acetylation conditions, a residual band was still present in the IR spectra at 3360 cm^{-1}. It was proved by chemical exchange with D_2O that this band at 3360 cm^{-1} was not due to water, nor to an unreacted alcohol function but rather to an overtone or a combination band. Azidation of a 100% acetylated PECH confirmed this last conclusion. At the same time, deuterium exchange experiments proved that acetylations under drastic conditions were completed for both linear and branched GAPs.

With the conditions for a complete acetylation of the alcohol groups found, the exact equivalent weight analysis by ^1H NMR was made using this derivative. The determination was applied on fourteen prepolymers with different structures including the branched GAP. The main imprecision found for this method was due to the difficulty of integrating the acetyl peak with a precision better than 5-10%. Due to the sharp acetyl peak, the sensitivity was increased by a factor of ten compared with the method using TFA or HFA. As with any other method, it was found that Ew greater than 5 000 were difficult to determine precisely with this method.

The only disadvantage over the IR method is that an acetylation reaction is required. Because of its precision, this method is now currently used at DREV in the development of propellants or explosives based on branched GAPs.

5.0 ACKNOWLEDGMENTS

The author wishes to thank Dr. L.-S. Lussier for his suggestions during the IR spectroscopy analysis of acetylated derivatives. Acknowledgments are also extended to Mr. Y. Boucher for his expert assistance and to Ms. A Gagnon for the acquisition of some IR spectra. The author wishes to especially thank Ms. N. Angers of Laval University who completed the acetylation study. Finally, thanks are also addressed to Dr. E. Ahad and Dr. G. Ampleman who provided the different GAPs.

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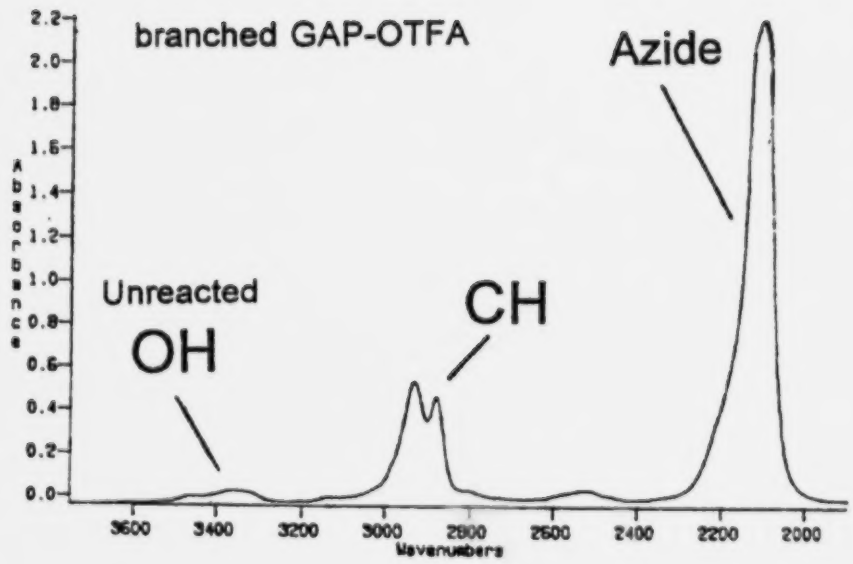


FIGURE 1 - IR spectrum of branched GAP acetylated by TFA derivative

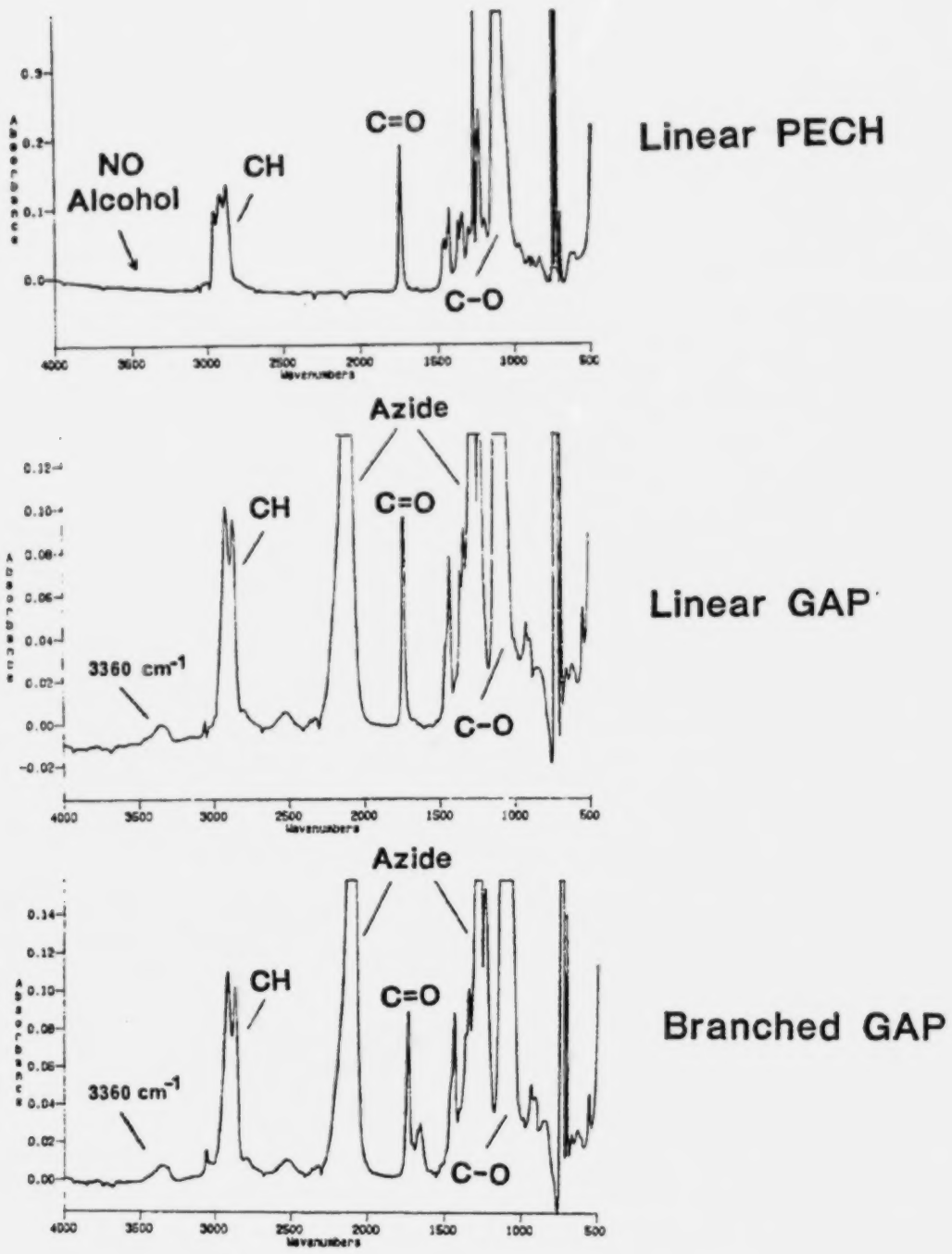
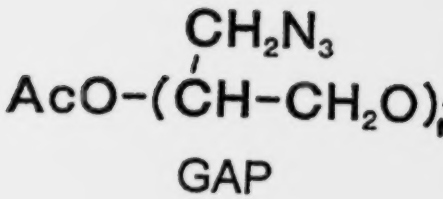


FIGURE 2 - IR spectra of linear PECH, linear GAP and branched GAP acetylated by drastic acetic anhydride/pyridine/ 95°C conditions



GAP

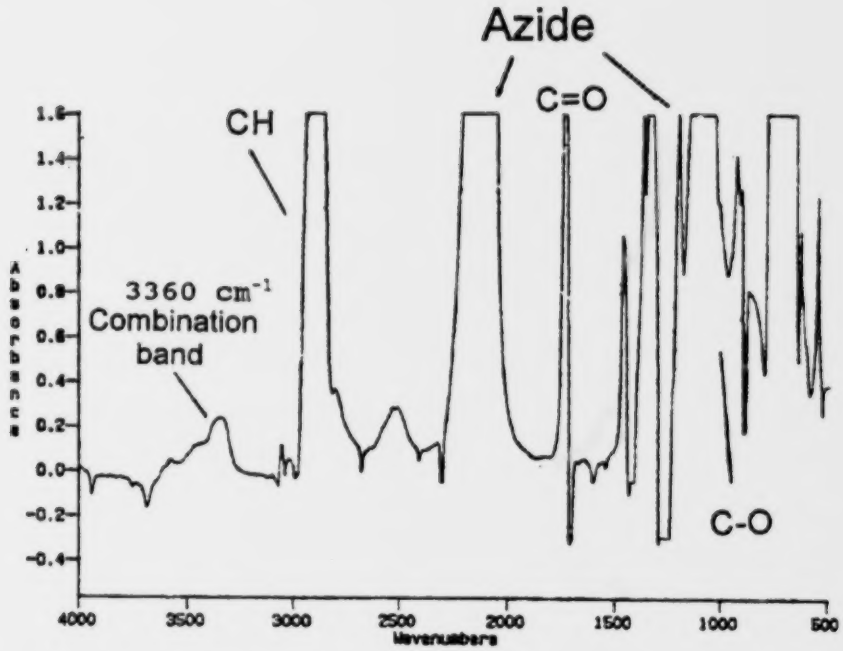
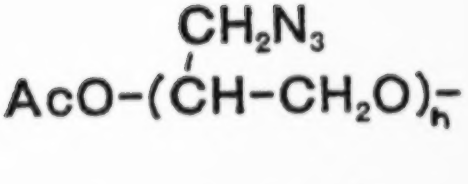


FIGURE 3 - IR spectrum of the 100 % acetylated linear GAP



branched GAP

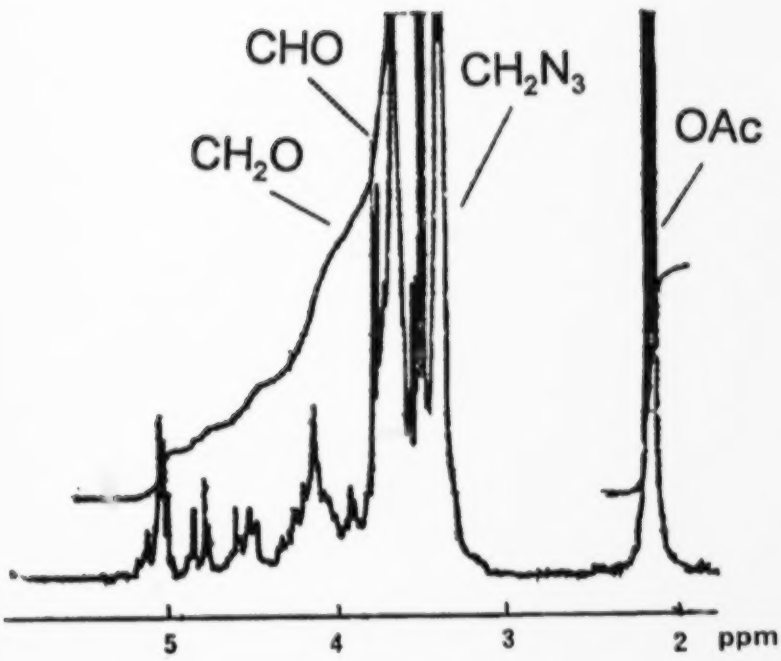
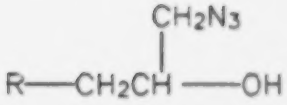
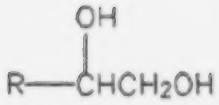


FIGURE 4 - ^{1}H NMR spectrum of acetylated branched GAP

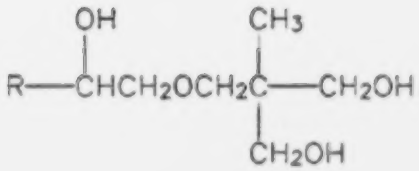
Linear



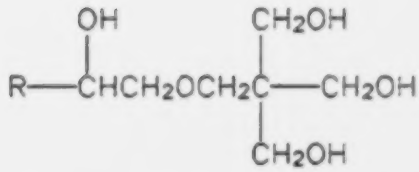
1 R=PECH
2 R=GAP



3 R=PECH
4 R=GAP

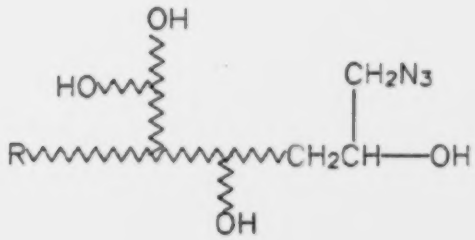


5 R=PECH
6 R=GAP



7 R=PECH
8 R=GAP

Branched



9 R=GAP

FIGURE 5 - Structure of the different prepolymers analysed by the equivalent weight method

TABLE I

Equivalent weights determined by the NMR method compared with the values by the IR method

Polymers		Equivalent Weight NMR Method	IR Method
HX-102	PECH 1[a]	1210	1180
Linear 1005-2	GAP 2[a]	1200	1175
Doubled	PECH 3[a]	600	------
Functionality	GAP 4[a]	680	------
Tripled	PECH 5[a]	420	------
Functionality	GAP 6[a]	430	------
Quadrupled	PECH 7[a]	310	------
Functionality	GAP 8[a]	360	------
Branched no.1[b]	GAP 9[a]	1500	1440
Branched no.2[b]	GAP 9[a]	2500	2240
Branched no.3[b]	GAP 9[a]	1340	1474
Branched no.4[b]	GAP 9[a]	2330	2033
Branched no.5[b]	GAP 9[a]	1245	1400
Branched no.6[b]	GAP 9[a]	333	------

a) Structure number, see Fig. 5.
b) Branched GAPs nos. 1 to 6 were synthetised with different procedures.

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